STRUCTURE OF GALVANIZED IRON

By WALTER ARTHUR and WILLIAM H. WALKER

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STRUCTURE OF GALVANIZED IRON.

By Walter Arthur and William H. Walker.

Galvanized iron, by which term in this article we shall include all zinc protected iron, consists not of a sheet of iron covered with a layer or skin of pure zinc, as one might expect, but, on the contrary, of a complicated system of iron-zinc compounds, starting with pure zinc on the outside and passing through these alloys to the iron base within. We shall consider the structure of zinc protected iron under the three heads:

1. Hot galvanized—material made by passing the iron through a bath of melted zinc.

2. Sherardized—the article heated in the presence of finely divided zinc and zinc oxide.

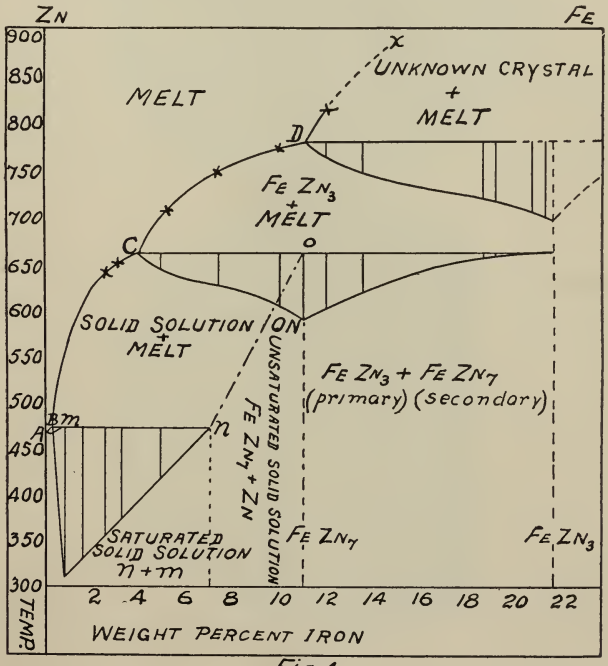

Fig. 1.

(Reprinted from the Journal of Industrial and Engineering Chemistry, Vol. 4, No. 6, June 1912.)

3. Wet or Electrogalvanized—a layer of either zinc or a zinc alloy deposited electrolytically on the iron article from an aqueous bath.

By examining the zinc-iron alloy diagram constructed by v. Vegesack,[1] which is reproduced in part as Fig. 1, we see that by

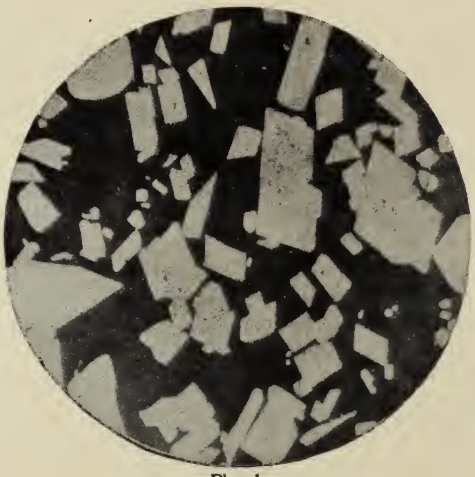

Plate 1.

raising the temperature iron will dissolve in melted zinc to at least 24 per cent. Beyond this point it is impossible to go, owing to the volatility of the zinc. Hence the composition of the crystals separating along the dotted line DX is not accu-

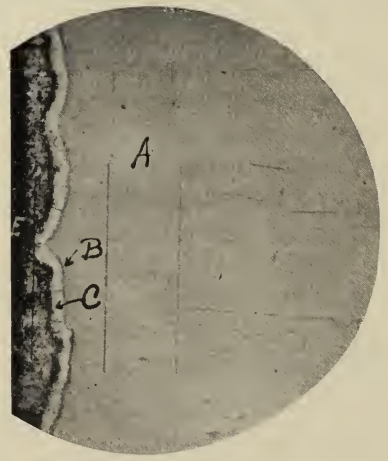

Plate 2.

[1] v. Vegesack, Zeit, anorg. Chem., 52, 30 (1907).

rately known, and will, for want of a better name, be called "binding alloy." From the molten mass at this point, crystals of this "binding alloy," $FeZn_3$, $FeZn_7$ (or a more or less saturated solution of zinc in $FeZn_7$), separate on cooling, the nature of the primary alloy depending on the concentration. The point *n* on the diagram represents the maximum solubility of zinc $FeZn_7$ and it is probably this saturated solid solution which is noticeable in certain sections of galvanized iron. A fraction of one per cent. (0. 5-0. 7 per cent.) of iron remains dissolved in the zinc after solidification.

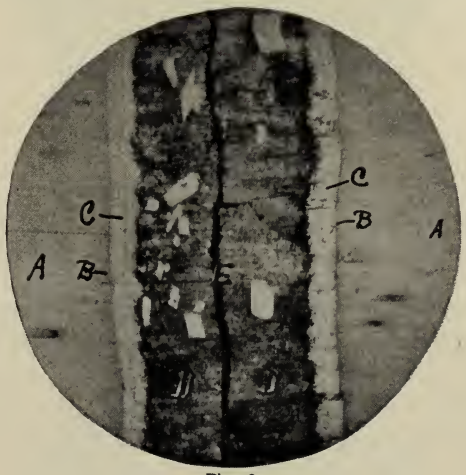

Plate 3.

Hot Galvanizing.—Consider first the ordinary method of galvanizing with reference to the equilibria indicated above. A piece of iron dipped into melted zinc at once begins to dissolve, the amount of solution depending on the length of time the iron is in the bath. As the solubility of iron in zinc is very low at this temperature the zinc bath soon becomes saturated, and a separation of the solid solution represented by the point *n* occurs. This crystalline compound is the "hard dross" of the galvanizer's bath and is shown in the photograph, Plate 1. There is also a tendency for equilibrium to establish itself on the surface of the iron, and as at this point of contract between molten zinc and solid iron all possible concentration may be considered to exist, the specific properties of the individual crystals determine

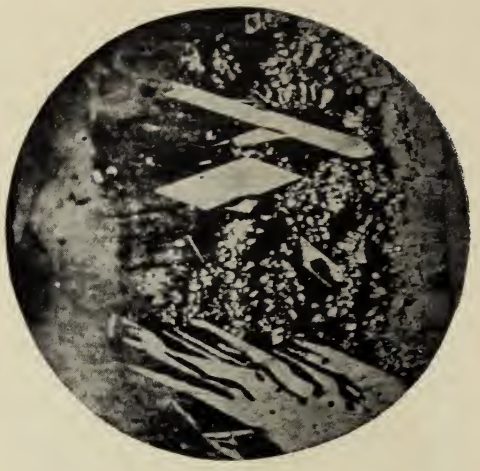

Plate 4.

the character and amount of each constituent. The actual behavior under varying conditions is best shown by microphotographs of the galvanized plates viewed in cross sections.

The preparation and polishing of plates in cross sections presented some difficulties, the chief of which lies in the tendency of the zinc to "flow" in polishing, and the ease with which it gives rounded or "burred" edges when cut at right angles. To prevent "burring" several strips of the iron were immersed in

Plate 5.

sodium silicate solution until the surfaces were thoroughly covered, clamped tightly together in a small hand vise and dried for about two hours at 100° C. The hardened sodium silicate

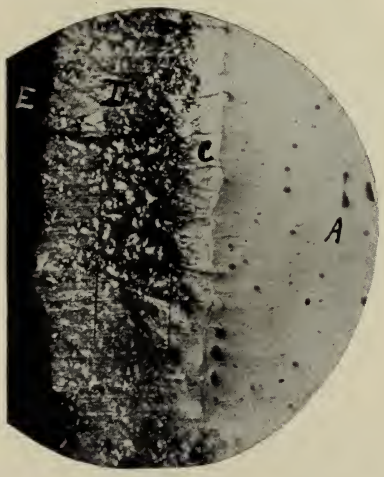

Plate 6.

served to fill out the interstices resulting from the unevenness of the galvanized iron surfaces, thus preventing the burring of

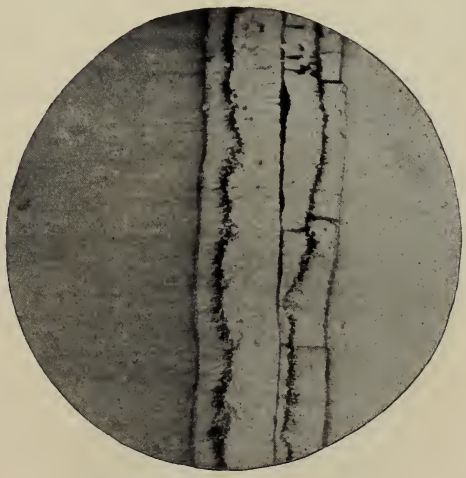

Plate 7.

the edges at such points and the filling of such spaces by zinc and iron particles in cutting and polishing. After the sodium silicate had thoroughly hardened, the edges of the pieces were

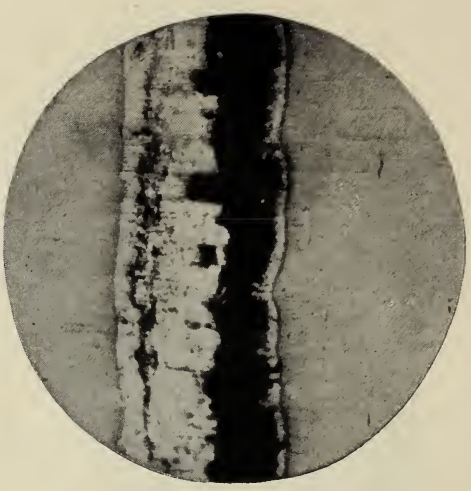

Plate 8.

all cut to the same plane by means of a fine file, the final strokes being made in alternate directions so as to prevent any flowing of the zinc. The file was followed by fine emery paper, and this by still finer emery paper until the edges presented an unscratch-

Plate 9.

ed surface to the unaided eye. The final polishing was done on soft cotton flannel, mounted on a piece of rubber, and covered with jeweler's rouge. In order to secure the best results, the

Plate 10.

final strokes were made very slowly and with a light pressure and always in alternate directions: 0.5 per cent. nitric acid in 95 per cent. alcohol was used as an etching reagent. By means of a micrometer eye piece the thickness of the various layers found in the etched specimens was measured. Each division of the scale shown in certain of the photographs represents 0.072 mm. on the specimen. Plate 2 shows a section of ordinary hot galvanized iron in which A is the iron, B a very thin layer of

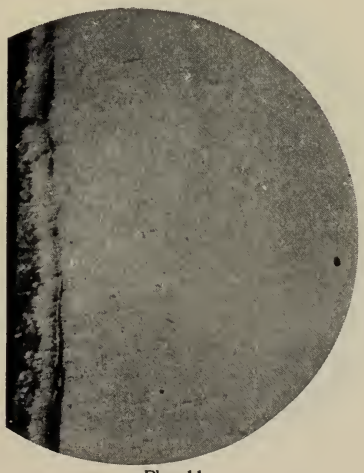

Plate 11.

the "binding alloy" of undetermined composition, C the compound $FeZn_3$, D the zinc layer which is filled with tiny crystals

Plate 12.

of $FeZn_7$, not visible in the photograph, and finally the sodium silicate. Plate 3 shows a section of heavily galvanized iron in which, because of a longer period of immersion in the zinc bath, much larger crystals of $FeZn_7$ have formed. The large increase in the amount of the compound $FeZn_7$ due to abnormally long immersion in the zinc bath is shown in Plates 4 and 5.

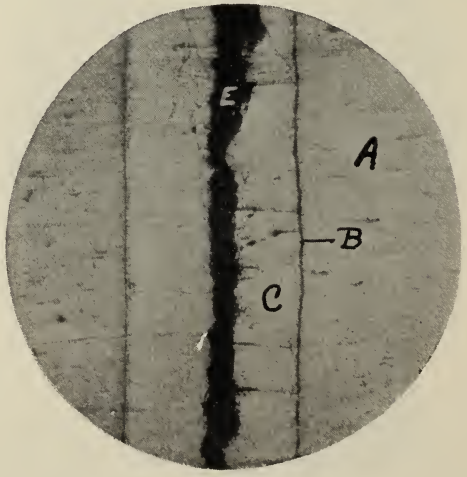

Plate 13.

That the tiny crystals of $FeZn_7$ are always present in the outer zinc layer can be determined in another way. If an ordinary galvanized plate is cautiously treated with caustic soda it is possible to dissolve the zinc without affecting the com-

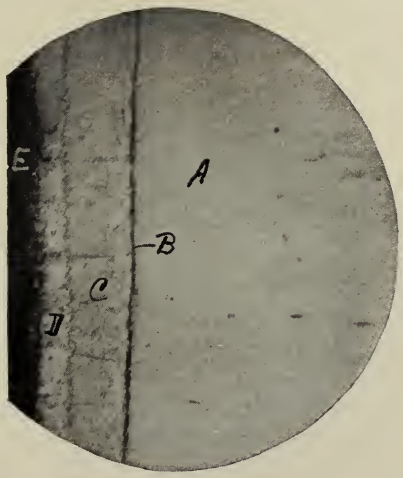

Plate 14.

pound. On a surface prepared in this way the tiny needle-like crystals of the compound become visible against the darker polygons of zinc.

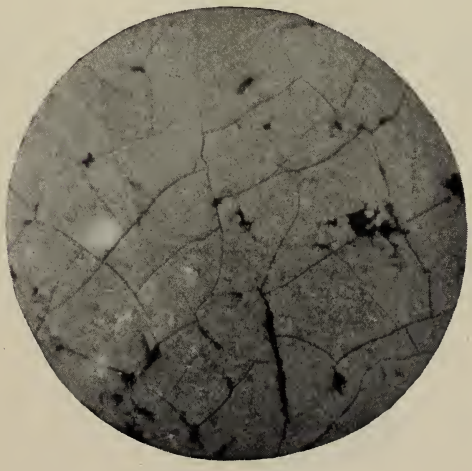

Plate 15.

Plate 6 is a cross section of a piece of galvanized pipe used and left by the French at Panama. It is remarkable that after an exposure of some thirty years there should still remain so unusual a coating of zinc. The layer of alloy $FeZn_3$ is also very heavy and the zinc is full of small crystals of $FeZn_7$, both facts indicating that the pipe was immersed for a considerable length

Plate 16.

of time in the galvanizing bath, and that the bath was fully saturated with $FeZn_7$.

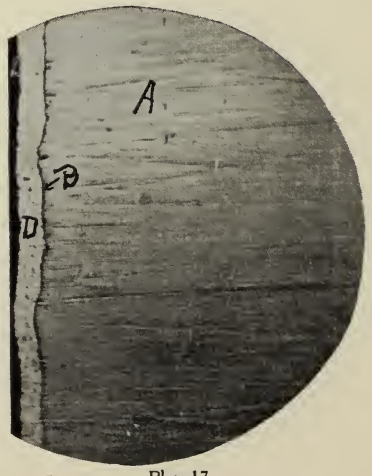

Plate 17.

Plate 7 is two pieces of ordinary galvanized iron, one very irregular in thickness, which have been so etched as to bring out more strongly the binding alloy B.

We have already corrected[1] a statement erroneously made by one of us[2] that these alloys were electronegative to iron. While not so electropositive as zinc, they are *not* electronegative, and hence afford a distinct protection to the iron base. Plate 8 represents two parts of a galvanized sheet which had been exposed to the weather for a number of years. The left side is from a

Plate 18.

spot which showed no corrosion, and exhibits a continuous layer of zinc on the alloy $FeZn_3$. The right side was selected from a spot very close to where corrosion of the iron had already commenced. Only the alloy is left and this is broken through at one or two points. Plate 9 shows two sections of heavily galvanized iron which had been allowed to rust in a damp place, but which have not been artificially etched. A is the rusted iron surface. B is a strip of iron surface next to the alloy which has been protected from corrosion by the electropositive character of the alloy. C is the alloy and D the zinc.

A property of galvanized iron with which all users are familiar is its tendency to crack and peal off when sharply bent. In-

[1]Patrick and Walker: This Journal, 3, Nov. 4 (1911).
[2]Walker: Proc. Am. Electrochem. Soc.

vestigation of cross sections made of specimens which had been bent showed that the parting of the galvanized coating from the iron takes place at the surface of the "binding alloy." This is as would be expected, inasmuch as the high iron alloys are very brittle. Such a break is shown in Plates 10 and 11.

Another property of galvanized iron is that of blistering with subsequent "flaking off" when heated, such, for example, as is seen on the flue of a house furnace. It was at first thought that the phenomenon was due to oxidation, but experiments carried on in an atmosphere of hydrogen and also carbon monoxide showed that this flaking occurred when the galvanized article reached a temperature of 360° C., or thereabouts. A polished section shows that in this case the parting takes place between the zinc and the alloy $FeZn_3$. Plate 12 shows such a structure. The black space between the alloy and the zinc is sodium silicate which has flowed in between the two layers.

Sherardized Iron.—The material known as sherardized iron is not a definite structure, but differs according to the temperature, time and composition of the zinc-powder mass employed. When the zinc powder is diluted with inert material, such as silica, and the time relatively short, the coating will consist of a very thin layer of the alloy $FeZn_3$, together with a more or less distinct layer of binding alloy of unknown composition. If the time is increased, and the powder richer in metallic zinc, a heavy coating is obtained as shown in Plate 13. If continued long enough, a layer of zinc forms on the surface of the alloy as shown in Plate 14. In all sherardized coatings are to be seen many cracks running through the alloy. This is particularly shown in the upper part of Plate 13. By polishing a section at right angles to the cross section, Plate 15 is produced. This shows the alloy to be broken into numberless fissures much resembling mud cracks. It is probable that greater study of etching methods would bring out still other alloys in this complicated structure. Thus Plate 16 shows two sherardized sections which have been etched by slow rusting in the air. They are from the same sheet as that used in Plate 13, and show a second alloy between the main coating alloy and what we have called the binding alloy. The blotched portions are the iron surfaces spotted with rust

flecks. Owing to the brittleness of the main alloy a regular outline at the sodium silicate surface is difficult to obtain.

Electrogalvanized Iron.—The metal deposited by an electric current depends upon the impressed voltage and the composition of the electrolyte or bath. A coating of very pure zinc may be produced, or an alloy of widely varying proportions of iron may be obtained by adding iron salts to the bath, or as is sometimes erroneously done, by using an iron anode. In any case a very thin binding alloy next to the iron is always to be seen. Plate 17 shows a piece of ordinary wet galvanized iron in which the coating D is pure zinc. E is the sodium silicate layer, and B the binding alloy. Plate 18 shows two pieces of such iron which have been bent before mounting. The coating is seen to have parted from the iron base along the line formed by it and the alloy.

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